(12) **EUROPEAN PATENT APPLICATION**

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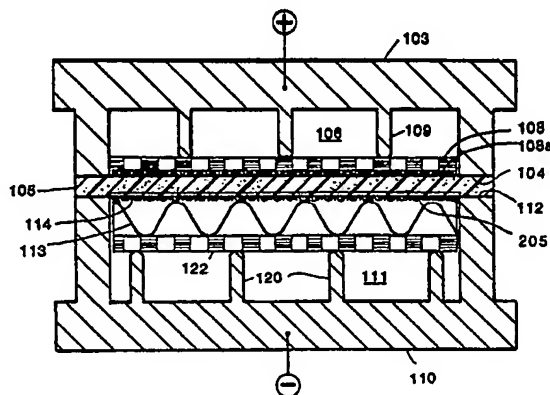(72) Inventor: De Nora, Oronzio, Piazza della Repubblica 19,
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(54) Method of generating halogen.

(57) Halogen is produced by electrolyzing an aqueous
halide in a cell comprising an anolyte chamber and a
catholyte chamber separated by a permeable membrane
or diaphragm (105). At least one electrode comprises
at least two sections. One section comprises a gas and
electrolyte permeable layer, sheet or mat (104) having
a catalytic surface, i.e. one having a low overvoltage.
This layer is spaced from the membrane (105) by a
second section comprising a thin intermediate electro-
conductive layer, screen or coating (205) which is in
contact with the membrane (105) on one side thereof,
the other side thereof being in contact with the main
cathode. This second or spacer section advantageously
has an electrode surface having a higher overvoltage
than the first electrode surface. Preferably the cathode
has the above construction.

EP 0 050 373 A1

Specification

The invention herein is directed to electro-lysis of an aqueous electrolyte and is particularly concerned with generating elemental halogen by electrolyzing an aqueous halide, such as hydrochloric acid or alkali metal chloride to generate elemental chlorine.

State of the Art

It is known to electrolyze aqueous alkali metal chloride or like halides in a membrane cell having an ion exchange (normally cation exchange) membrane which separates anode from cathode. Since the membrane itself is generally imperme-able or substantially so to gas and liquid flow, the electro-lysis generates chlorine at the anode and alkali at the cathode, the alkali being of high purity and containing only very low chloride concentration.

One type of cell which has been proposed for such electro-lysis is the solid polymer electrolyte cell.
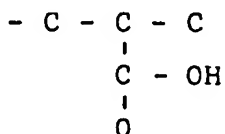
A solid polymer electrolyte cell is characterized by an ion exchange membrane, which separates the electrodes of the cell and by the fact that one or preferably both electrodes are in contact with the membrane. The solid polymer electrolyte cells present (with respect to conventional membrane cells in which the cathode and frequently both anode and cathode are separated from the membrane), several advantages useful in different electrolysis processes. More precisely :

1) The overall voltage between electrodes is lower because the interelectrodic distance is reduced practically to the membrane thickness.

2) The so-called "bubble effect" is eliminated or at least
    minimized, i.e. the difficulty normally encountered in
    electrolytic processes where gas   evolved at the electro-
    de accumulates in the zone between electrodes is avoided
    because evolved gas can be released behind the electrodes
    to the inside of the cell compartment.

3) The cells may be very compact and thus the ohmic drops
    at the current distribution structures can be reduced.

The ion permeable diaphragms are cation exchange polymers
in the form of thin flexible sheets or membranes. Generally,
they are imperforate and do not permit a flow of anolyte into
the cathode chamber but it   has also been suggested that
such membranes may be provided with some small perforations
to permit a small flow of anolyte therethrough, although the
bulk of the work appears to have been accomplished with imper-
forate membranes.

Typical polymers which may be used for this purpose include
fluorocarbon polymers such as polymers of trifluoroethylene
or tetrafluoroethylene or copolymers thereof which contain
ion exchange groups.   The ion exchange
groups normally are cationic groups including sulfonic acid,
sulfonamide, carboxylic acid, phosphoric acid and the like,
which are attached to the fluorocarbon polymer chain through
carbon and which exchange cations. However, they may also
contain anion exchange groups. Typical such membranes have
the general formula :

$$- C - C - C - C \quad \text{or}$$
$$ |$$
$$ C$$
$$ |$$
$$ SO_3H$$

$$- C - C - C$$
$$ |$$
$$ C - OH$$
$$ |$$
$$ O$$

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Such membranes include typically those fluorocarbon ion exchange polymers manufactured by the Du Pont Company under the trade name   "Nafion" and by Asahi Glass Company of Japan under the trade name   "Flemion". Patents which describe

5 such membranes include British Patent No. 1,184,321 and U.S. Patent No. 3,282,875 and U.S. No. 4,075,405.

Since these diaphragms are ion permeable but do not permit anolyte flow therethrough, little or no halide ion migrates through the diaphragm of such a material in an

10 alkali chloride cell and therefore the alkali thus produced contains little or no chloride ion. Furthermore, it is possible to produce a more concentrated alkali metal hydroxide in which the catholyte produced may contain from 15 to 45% NaOH by weight or even higher. Patents which describe such a process

15 include U.S. Patents No. 4,111,779 and No. 4,100,050 and many others. The application of an ion exchange membrane as an ion permeable diaphragm has been proposed for other uses such as in water electrolysis.

In cells of the type contemplated, the cathode is in

20 close proximity to or in direct contact with the ion exchange membrane. They must be sufficiently permeable to permit rapid escape of evolved gas from the points of their evolution and to provide ready access of liquid electrolyte to these points as well as rapid removal of evolved alkali or other electro-

25 lysis products produced from such points. Thus the electrodes are normally quite porous.

According to a well-known method of providing such an electrode, electrode material in the form of very fine powder of catalytic material, i.e. platinum group metal or oxide is

30 mixed with an inert polymeric binder, mainly polytetrafluoro-ethylene (PTFE).

The mixture is sintered and hot-pressed in a suitable mold, in the form of an/extremely thin and sufficiently coherent porous film or layer . Said films are then hot-pressed onto the membrane surface to obtain a permanent adhesion to the membrane.

5 Methods of producing such electrodes are described in certain patents assigned to the General Electric Company. One patent which describes such methods is U.S. Patent No. 3,297,484.

According to another method, it is possible to deposit an adherent and porous layer of metal resistant to corrosion

10 and electrocatalytic on the membrane surface, which may or may not be preroughened by chemical reduction and deposition of the metal from solutions. Said methods are defined "electroless" to distinguish them from the galvanic deposition. This method is described in the Italian Patent Applications SNs

15 24829 A/79 and 20489 A/80.

One difficulty which has been encountered with permeable cathodes which are in direct contact with or bonded to the membrane is that cathodic efficiency is relatively low, for example 85% or below and that oxygen in appreciable concentrat-

20 ion, for example above 0.5 to 1% or more by volume, is evolved in the chlorine produced.

Apparently some portion of the alkali metal hydroxyl evolved at the cathode tends to migrate through the membrane. This may be due to the fact that caustic soda produced at the

25 interface is not sufficiently and uniformly diluted by the catholyte within the cathode compartment of the cell.

The high alkalinity may induce dehydration of the membrane with consequent decrease of the electrical conductivity, moreover the high concentration gradient increases the back-diffus-

30 ion of the hydroxyl ion toward the anode with a resulting loss of the faraday efficiency.

The creation of varying gradients of alkalinity on or in the membrane may cause membrane shrinking and membrane swelling in localized areas and continual changing of these events and this may result in detachment and/or loss of cathode layer or cathodic material. Whatever the actual mechanism, the adverse results referred to above accrue.

Attempts have been made to avoid these problems by using a membrane which has a weaker acidic section or surface on the cathode side and on the anode side. For example membranes have been provided wherein the anode side comprises sulfonic or phosphonic groups and the cathode side comprises a cation exchange layer in which the acid groups are largely or even completely carboxylic. In another embodiment the membrane is sulfonic acid or salt thereof on the anode side whereas on the cathode side the membrane surface is largely sulphon-amide.

In an effort to reduce the cost of constructing such cells and perhaps to simplify their construction, foraminous electrodes (screens foils or the like) which are not bonded to the membrane have been tested. However, it has been noted that this has been accompanied by an increase in cell voltage. This is particularly true when more concentrated alkali containing 25 percent by weight or more of NaOH or equivalent alkali is produced.

THE INVENTION

According to this invention halogen is effectively generated by electrolyzing an aqueous halide in an electro-lytic cell having a pair of opposed electrodes separated by an ion permeable separation preferably an ion exchange polymer and where at least one electrode, preferably the cathode, has two surfaces. The first surface is resistant to electrodic

and electrolytic attack and has a low overvoltage being readily
capable of functioning as an electrode and evolving electro-
lysis product by electrolysis. The second such surface has
a higher overvoltage (hydrogen overvoltage in the case of the
5   cathode surface or chlorine overvoltage in the case of anode
surface) and is between the lower overvoltage surface and the
membrane, generally being in direct contact with or even
bonded to the membrane. Of course both surfaces are electro-
conductive and are capable of being polarized as an electrode.
10   Furthermore both surfaces are in direct electrical contact
so that there is little or substantially no potential difference
between them.

     As a typical embodiment the cathode may comprise an
electroconductive porous metal coating disposed on and bonded
15   to the cathode side of the membrane. Alternatively, the
intermediate cathode section may be in the form of an electro-
conductive grid or grate with relatively high hydrogen over-
voltage electroconductive surface which is pressed against
the cathode side of the membrane.

20   Since the first or rear most cathode section has a lower
hydrogen overvoltage surface than that of the front coating
or grid engaging the membrane a major portion and even
substantially all of cathodic electrolysis occurs at points
spaced by the spacer or barrier from the membrane as distinguish
25   ed from on or close to the membrane surface.

     The cathode where the major electrolysis takes place
is readily porous and permits ready flow including lateral
flow of catholyte therethrough. Thus it may be in the form
of fine mesh flexible electroconductive metal screen having
30   5 to 10 mesh openings per centimeter or a mat of undulating
wire screen or a combination of these elements. The openings
are relatively large and thus provide channels adjacent to

the points of contact between the conductive spacer and the
main cathode section whereby catholyte may flow edgewise
along the cathode surface and adjacent these points thereby
sweeping away evolved alkali from the front portion of the
cathode as well as from the areas more remote from the
membrane.

The spacer, barrier or intermediate section is itself
quite thin often being less than 5 microns. In contrast the
remaining active section is at least 100 microns thick and
this is two or more or even 10 or more times the thickness
of the spacer. This permits flowing catholyte to have access
to the front portions of the cathode a distance only equal to
the spacer thickness thereby reducing the probability of local-
ized high alkali concentrations undergoing formation at the
membrane surface. Where the spacer is of the same or substantial-
ly the same surface composition as the main cathode section
some electrolysis may take place on the spacer or in the pores
thereof. This amount is reduced by providing a barrier or
spacer of higher hydrogen overvoltage than the hydrogen over-
voltage of the major active cathode area.

For example, the more active cathode may have a surface
comprising a platinum group metal or oxide thereof which has
a very low hydrogen overvoltage. In that case the intermediate
layer can have an electroconductive surface of a metal or
oxide which is higher in overvoltage. A thin porous layer
of silver or copper metal or an iron or nickel screen may be
used for this purpose. As will be understood other conductive
materials which are resistant to corrosion in the alkaline
cathode area may also be used.

The intermediate section in any case is porous and perme-
able to electrolyte. Being quite electroconductive, it may
co-operate in transmitting current to the more remove active
cathode areas without serious increase in overall voltage.

In one effective embodiment the intermediate cathode
section comprises a thin porous film of silver particles
deposited on the membrane surface for example by chemical
reduction or electroless deposition. The ratio between empty

5   and solid spaces in such a deposit or layer often ranges from
1.2 to 0.5.

In the practice of this method one surface of the
membrane is roughened by sandblasting or other method and then
the roughened surface is swelled or hydrated with an alkali

10   mild hydroxide solution, preferably diluted aqueous caustic
soda or aqueous potash. The alkali treated surface is contact-
ed with a salt solution of the metal to be deposited, prefer-
ably silver in the form of a reducible compound such as silver
nitrate; the membrane is then contacted with a solution

15   containing hydroquinone.

The hydroquinone, due to the high alkalinity existing
at the surface of the membrane, previously treated with the
alkali solution, oxidizes the quinone reducing the metal ions
absorbed on the membrane surface to metal.

20   The reduction proceeds until the alkalinity at the
membrane surface falls. The reduction progresses only while
adequate soda or potash is available at the membrane surface
to neutralize evolved hydrogen ion or acidity generated with
the oxidation of hydroquinone to quinone. The reduction

25   stops as the alkalinity due to the soda or potash previously
absorbed on the membrane is consumed and the pH of the surface
proceeds to or toward neutrality or an acidic state.

Due to this fact, the metal grains formed at the surface,
do not act as catalytic sites for a further reduction of the

30   metal and the coating thus obtained is finely dispersed
highly porous and uniform, with metal grains therein being
very small and the coating is quite thin.

As the amount of the deposited metal is strictly determined by the availability of caustic soda and potash in the surface layer of the membrane, it is possible to control the amount and depth of deposited metal by limiting the depth of penetration of soda or potash within the membrane and contacting the pretreated membrane with the solution of the salt of metal to be reduced and then with the solution containing hydroquinone in quick succession.

According to the preferred method one surface of the hydrated membrane is brought in contact with the caustic solution for a time comprised between 30 and 120 seconds, only on the surface to be treated, so that the diffusion of the soda or potash with the membrane takes place at largely or completely the surface whereon the electrode has to be applied.

Usually, the temperature is the room-temperature, although other temperatures may be considered as well.

The concentration of the caustic solution is another determining factor on the depth of penetration of the soda or potash within the thickness of the membrane. A diluted solution tends to swell more the membrane and therefore to facilitate the penetration of soda or caustic. On the contrary, a concentrated solution tends to shrink the membrane, making it more impervious to the internal diffusion of soda or potash.

Preferably, the aqueous alkaline solution used in a soda solution between 2.5 and 20% by weight of NaOH. The diffusion of soda within the membrane is therefore controlled by adjusting the contacting time through the concentration of the solution and the temperature. When the alkali absorption is effected, the membrane surfaced is promptly rinsed with deionized and distilled water, and then contacted with the solution of the metal salt to be reduced. Preferably, this is a solution of silver nitrate with normality between 0.01 and

1 N, more preferably between 0.1 and 0.5 N. The temperature
is the room temperature, though different temperatures may be
considered.

Usually, the treating times for this metal salt range
from 30 to 120 sec., considering that a diluted solution
requires a time longer than a more concentrated solution.

The membrane is again rinsed and the surface treated with
alkali and then silver salt is contacted with an aqueous
solution containing from 10 to 30% of a reducing agent which
reduces the metal salt and generates hydrogen ion, such as
hydroquinone, for a time ranging from 1 to 15 minutes.

Other modifications of the preferred method hereinabove
described are also possible. For example, the membrane may be
contacted with soda on both surfaces, whenever it is desired
to apply the electrode coating on both surfaces, before
proceeding to the reduction with hydroquinone.

Alternatively, other alkali solutions may be used, such
as sodium carbonate, or potassium carbonate solutions.

The coatings obtained with this embodiment of the present
invention are exceptionally uniform with a thickness which
may range from 0.025 to 0.5 micron the thickness being largely
controlled by controlling the depth of penetration of the alkali
and the subsequent absorption of metal salts. The lateral
resistivity of the metal films thus obtained may range between
0.5 to 10 Ohm centimeters.

While the silver film appears continuous to the naked
eye, pores or channels extend through its thickness so that
the alkali cations are readily transferred through the film
as well as the membrane.

The use of a reducing agent such as hydroquinone which
generates hydrogen ion in the course of reducing metal salt
to metal is especially effective where it is desired to apply

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a metal coating to a cation exchange membrane and to avoid metal deposition within the interior of the membrane sheet. Since the cation exchange material is itself acidic except to the extent where the exchange groups have been neutralized any generation of hydrogen ion reduces pH. Where as in the case of hydroquinone reduction the metal salt reduction takes place only under an alkaline pH, the reduction stops as the alkalinity falls. Hence, if only the surface is contacted with alkali for a time insufficient to allow substantial alkali penetration below the surface reduction of metal is restricted to the depth of alkali penetration.

The invention is particularly applicable to diaphragms or membranes wherein one side or face thereof is less acidic or comprises a weaker acid than the other. For example, in the case of a membrane having predominately sulfonic groups on one side and predominately carboxylic groups on the other side, an effective silver coating is applied to the weaker acid side, i.e. the carboxylic side. Similarly, where the membrane is sulfamid on one side and sulfonic on the other, the coating is applied to the weaker acid side, i.e. the sulfonamid side. Of course the carboxylic side may also contain some sulfonic groups, if desired.

At all events the membrane is thus coated with a thin electroconductive porous layer bonded thereto at least on one face. This membrane is installed in a cell with the coating on the cathode side. Such a cell has an electroconductive cathode section which is installed to bear against the above silver coating on its rear face (face remove from the membrane) and this cathode section has a lower hydrogen overvoltage than the porous silver coating.

According to a further embodiment the intermediate cathode section may comprise a screen or grid which is open to electrolyte and gas flow and which is merely pressed against or even

embedded in the membrane so long as electrolyte has free access to its surface and evolved gas can escape therefrom. Ordinary iron or nickel screen or graphite cloth which is thin and flexible so that it can bend to accomodate for irregularities in the membrane contour and can permit free electrolyte flow may be used for this purpose. Such screens are electroconduct- ive and have a surface which can function as a cathodic surface but at a higher voltage because of its high hydrogen over- voltage surface.

This screen is backed by the first or principal cathode screen which may be in the form of one or a stack of electro- conductive screens and/or and electroconductive compressible wire mat which has a lower overvoltage surface than the intermediate screen. Generally, the electrode area of the low overvoltage surface substantially exceeds often by 25-50% or more the electrode area of the higher overvoltage surface of the front or intermediate cathode section.

According to a further embodiment, the cathode may comprise a single structure such as a compressible electro- conductive mat or a screen or grill work with two electro- conductive electrode surfaces one of which has a lower hydrogen overvoltage aligned with respect to the membrane so that the high overvoltage surface bears against the membrane with the lower overvoltage surface being spaced therefrom.

In all of the above embodiments the higher overvoltage cathode surface may comprise metallic iron or nickel or silver, silver alloy etc., while lower overvoltage surface may comprise a platinum group metal or electroconductive oxide (platinum, ruthenium, palladium etc.) as a coating on a nickel or iron screen as an alloy or mixed oxide of such platinum group metal and nickel. Also such lower overvoltage surface may comprise a conductive sulfide such as nickel or iron sulfide

or mixtures thereof with iron or nickel metal or oxide.

Generally the difference in hydrogen overvoltage between the two surfaces should not be excessive and preferably they do not differ by more than about 0.5 volts at current densities in the range of 2 to 5 KA/m^2 and preferably comprised between 0.1 and 0.5 volts.

If desired, the membrane surface may be roughened or abraded, for example by sandblasting, sputter etching, embossing or other means to increase its surface area. The cathode is then pressed into unbonded contact with such rough surface.

In such a case the surface area of the abraded surface of a membrane of given size generally is at least about 25 percent and often 50% of above greater than the surface area of a membrane of such size or dimension with a smooth surface. For example, a square membrane sheet one meter square has an overall or enclosed area of one square meter. However, by adequate sandblasting, the sheet may be roughened enough to increase its surface area to 1.25 - 1.5 square meters or even higher although the overall area or its bulk edge to edge cross sectional area enclosed by the periphery of the sheet remains the same.

Generally the depth of penetration of the pitted or rough- ened area is small, rarely exceeding about 25 micron and generally the depth of the roughened area is below 10 microns, generally being below 5 microns. Also the average distance between crests of the roughened area is small, rarely exceed- ing 50 microns and preferably being below 10 microns, usually being 0.1 to 5 microns.

The roughening of the membrane surfaces may be achieved by sandblasting the membrane with sand or quartz particles of 50 to 150 microns for a few seconds up to one or two minutes.

Also it may be accomplished by cathode sputter etching
or by embossing the sheet or by casting the sheet in contact
with a roughened mold surface.

The invention herein contemplated may be applied to
an electrolytic cell such as the one diagrammatically illustrat-
ed in the accompanying drawing in which:

Fig. 1 is a diagrammatic horizontal sectional view of
the cell having the double surfaced electrode installed
therein, and

Fig. 2 is a diagrammatic vertical sectional view of
the cell of Fig. 1.

As shown, the cell comprises an anode end plate 103
and a cathode end plate 110, both mounted in a vertical plane
with each end-plate in the form of a channel having side
walls respectively enclosing an anode space 106 and a cathode
space 111. Each end plate also has a peripheral seal surface
on side-walls projecting on each side of the cell from the
plane of the respective end plate, 104 being the anode seal
surface and 112 being the cathode seal surface. These surfaces
bear against a membrane or diaphragm 105 which stretches
across the enclosed space between the side walls separating
anode from cathode. In one embodiment, this membrane is
provided on the cathode side with the roughened surface with
a cathode screen bearing against the rough surface. In another
the membrane may be coated with silver, copper or the like
porous coating 205 as described above.

The anode 108 may comprise a relatively rigid uncompress-
ible sheet of expanded titanium metal or other perforate,
anodically resistant substrate, preferably having a non-
passivable coating thereon such as a metal or oxide or mixed
oxide of a platinum group metal. This sheet is sized to fit
within the side walls of the anode back plate and is supported

rather rigidly by spaced electroconductive metal or graphite
ribs 109 which are fastened to and project from the web or
base of the anode end plate 103. The spaces between the ribs
provide for ready flow of anolyte which is fed into the bottom
and withdrawn from the top of such spaces. The entire end
plate and ribs may be of graphite and alternatively, it may
be of titanium clad steel or other suitable material. The
rib ends bearing against the anode sheet 108 may or not be
coated, e.g. with platinum or like metal to improve electrical
contact and the anode sheet 108 may, if desired, be welded
to the ribs 109. The anode rigid foraminous sheet 108 is held
firmly in an upright position. This sheet may be of expanded
metal having upwardly inclining openings 10 directed away
from the membrane (see Fig. 2) to deflect rising gas bubbles
towards the space 109 and away from the membrane.

More preferably, a fine mesh pliable electrolyte permeable
screen 108a of titanium or other valve metal coated with a
non-passivatable layer which is advantageously a noble metal
or conductive oxides having a low chlorine overvoltage for
the anodic reaction (e.g. chlorine evolution), is disposed
between the rigid foraminous sheet 108 and the membrane 105.
The screen 108a usually a fine mesh screen provides a density
of contacts of extremely low area with the membrane in excess
of at least 30 contacts per square centimeter. It may be spot
welded to the coarse anode screen 108 or not, as desired.

On the cathode side, ribs 120 extend outward from the
base of the cathode end plate 110 a distance which is a
fraction of the entire depth of the cathode space 111. These
ribs are spaced across the cell to provide parallel space
for vertical electrolyte flow from bottom to top and engage
the cathode which is in sheet or layer form, i.e. it's thick-
ness dimension is much less than its width and height. The
cathode end plate and ribs may be made of steel or a nickel

iron alloy or other cathodically resistant electroconductive material. On the conductive ribs 120 is welded a relatively rigid pressure plate 122 which is perforate and readily allows circulation of electrolyte from one side thereof to the other. Generally these openings or louvers are inclined upward and away from the membrane or compressible electrode toward the space 111 (see also Fig. 2). The pressure plate is electroconductive and serves to impart cathodic polarity to the electrode and to apply pressure thereto and it may be made of expanded metal or heavy screen of steel, nickel, copper or alloys thereof.

A relatively fine flexible screen 114 bears against the rough surface of the membrane or against the coating 205, if present on the cathode side of the active area of diaphragm 105. This screen because of its flexibility and relative thinness, assumes the contours of the diaphragm and therefore that of anode 108. A metal screen mat 113 is disposed behind the screen and this compressible mat is cathodic and serves as part of the cathode. The screen 114 is composed of nickel wire or other electroconductive cathodically resistant wire which has a surface of low hydrogen overvoltage (lower than the silver) and may be coated with a low hydrogen overvoltage coating such as coating of a platinum group metal or oxide thereof.

Preferably two or more electroconductive metal screens are interposed between the rough membrane surface and the compressible mat 113. In such a case it is often advantageous to provide a screen of relatively higher hydrogen overvoltage in direct contact with the membrane surface and a second screen or bank of screens which have a surface or relatively lower hydrogen overvoltage behind but in contact with the higher overvoltage screen. In that case the high overvoltage screen surface may be of iron or steel or nickel whereas the

surface of the more remote screen or screens may comprise a
coating of platinum group metal or conductive oxide thereof
or nickel sulfide or other low overvoltage coating. Usually
the differential in hydrogen overvoltage between the two

5   types of surfaces ranges from 0.05 to 0.5 volts, rarely
being above 0.6 volts. Of course the screen surfaces are in
close electrical contact with each other since the screens
are pressed tightly together and against the membrane by the
compressible mat and are essentially at the same electrical

10 potential.

The screens advantageously are fine in mesh and provide
many contacts of low area with the membrane and with the next
adjacent screen, usually being at least 30 contacts per square
centimeter. A compressible electroconductive wire mat 113 is

15 disposed between the cathode screen 114 and the cathode
pressure plate 122.

As illustrated in Fig. 1, the mat 113 is a crimped
corrugated or wrinkled compressible wire-mesh fabric which
fabric is advantageously an open mesh knitted-wire mesh of

20 the type described in U.S. application for United States
Letters Patent Serial No. 102629 filed December 11, 1979
wherein the wire strands are knitted into a relatively flat
fabric with interlocking loops. This fabric is then crimped
or wrinkled into a wave or undulating form with the waves

25 being close together, for example 0.3 to 2 centimeters apart,
and the overall thickness of the compressible fabric is 2 to
10 millimeters. The crimps may be in a zig-zag or herringbone
pattern and the mesh of the fabric is coarser, i.e. has a
larger pore size than that of screen 114. Both the screen

30 114 and the mat generally have pore or void size substantially
larger than the pore size of coating 205.

As illustrated in Fig. 1, this undulating fabric 113 is disposed in the space between the finer mesh screen or screens 114 and the more rigid expanded metal pressure plate 122. The undulations extend across the space and the void ratio

5   of the compressed fabric is, notwithstanding compression, preferably higher than 75%; preferably between 85 and 96%, of the apparent volume occupied by the fabric. The waves extend in a vertical or inclined direction so that channels for upward free flow of gas and electrolyte are provided which

10   channels are not substantially obstructed by the wire of the fabric. This is true even when the waves extend across the cell from one side to the other because the mesh openings in the sides of the waves permit free flow of fluids.

The end-plates 110 and 103 are clamped together and bear

15   against membrane 105 or a gasket shielding the membrane from the outside atmosphere disposed between the end walls. The clamping pressure compresses the undulating fabric 113 against the finer screen or screens 114 and the metal coating or the roughened membrane to the thickness substantially less than

20   the fabric in it uncompressed state. This in turn presses the screen 114 against the membrane and thus, the anode surface of the membrane presses against anode 108a.

In the operation of this embodiment, substantially saturat-ed sodium chloride aqueous solution is fed into the bottom

25   of the anolyte compartment of the cell and flows upward through channels or spaces 105 between ribs 109 and depleted brine and evolved chlorine escapes from the top of the cell. Water or dilute sodium hydroxide is fed into the bottom of the cathode chamber and rises through channels 111 as well as

30   through the voids of the compressed mesh sheet 113 and evolved hydrogen and alkali is withdrawn from the top of the cell.

Electrolysis is caused by imparting a direct current electric potential between the anode and cathode end plates.

As shown in Fig. 2, at least the upper openings in pressure plate 122 are louvered to provide an inclined outlet directed upwardly away from the compressed fabric 113 whereby some portion of evolved hydrogen and/or electrolyte escapes to the rear electrolyte chamber 111. Therefore, the vertical spaces at the back of the pressure plate 122 and the space occupied by compressed mesh 113 are provided for upward catholyte and gas flow.

By recourse to two such chambers, it is possible to reduce the gap between pressure plate 122 and the membrane and to increase the compression of sheet 113 while still leaving the sheet open to fluid flow and this serves to increase the overall effective surface area of the active positions of the cathode.

According to the improved method of this invention for the electrolysis of sodium chloride, aqueous brine containing from 140 to 300 grams per liter of sodium chloride is circulated within the anode compartment of the cell. Chlorine is evolved at the anode, while the solvated ions tend to migrate through the cation membrane and reach the cathode where caustic soda of substantial concentration above 15-20% by weig·· and hydrogen is evolved. Solutions containing 25 to 40% by weight of alkali metal hydroxide may be produced with anode and cathode efficiencies above 90% frequently above 95%.

It will be seen that the cathodically polarized section includes the end plate 110 and pressure plate 122 mat 113 and the screen or assembly of screens 114 which bear against the membrane.

The screen or the rear screen and/or the mat 113 is coated with a coating or surface which has a low or substantially negligible hydrogen overvoltage. Typical coatings include

a mixture of nickel and conductive ruthenium oxide, platinum
black or platinum metal or other such coating of a low hydrogen
overvoltage material. The depth of this active area may be
expanded by coating the compressible wire fabric 113 with

5   the same material.

Since electrolyte flow is rapid through the compressed
fabric 113 and the mesh of the screen 114, a large portion
of the sodium hydroxide produced may be evolved a distance
away from the membrane surface and is removed by the flowing

10   electrolyte.

In the embodiment where the membrane is provided with a
thin porous metal coating of silver, copper or the like the
coating becomes polarized as a cathode. However, generation
of caustic and chlorine at such coating is small or even

15   substantially nonexistent relative to the amount generated on
the screen 114 and or compressed fabric 113 for at least two
reasons, first it has a higher hydrogen overvoltage than the
surface on screen 114 or 113 and second because its area is
comparatively smaller because it has a thickness less than 1

20   to 2 microns as discussed above. Consequently, only a small
portion of the evolved caustic tends to back migrate toward
the anode.

The thin silver layer may thus constitute a less active
porous spacer element between the membrane and a more active

25   cathode area where the bulk of the caustic is generated and
swept away. This more larger active area is readily permeable
to edgewise electrolyte flow promoting rapid removal of
caustic not only from the active cathode surfaces but from
the pores of the thin silver coating.

30   If the silver coating is thickened the path of flow of
evolved caustic through the coating is lengthened thus hinder-

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ing although not necessarily completely preventing escape of
caustic evolved therein. However, this may tend to promote
the undesirable back migration discussed above. Thus it has
been considered desirable to limit thickness of the layer to

5   a maximum of 2 to 5 microns preferably not over 2 microns and
more advantageously below one micron.

The active screen as well as the fabric 113 have openings
much larger than the pores of the silver coating. Thus such
openings may be 0.1 centimer wide or even more and in case

10   of the fabric 113 the voids exceed the solid wire sections
by several times. As a consequence electrolyte may flow in
an edgewise direction through fabric 113 as illustrated in
Fig. 2 as well in a ramdom path around, along and through
the open mesh of screen 114.

15   It will be understood that other embodiments of the
invention may be provided. While a silver coating having a
thickness below one micron, usually below 0.5 micron, is
especially effective in promoting cathode efficiency of 95%
or above, the silver coating may be thickned as by electro-

20   deposition or further electroless coating so long as good
porosity of the coating is retained. Generally, however, this
coating is less than about 5 microns and rarely above one or
two microns in thickness.

Although the metal coating 205 is porous, the coating

25   may appar continuous to the naked eye. Thus the pores or voids
are much smaller than those in either the screen or the mat.
This small pore size may be the reason the coating appears to
be a barrier which may restrain back migration of alkali to the
area of the anode.

30   At all events the cell is capable of operation at cathode
Faraday efficiencies of 95% and above with less than 0.5% if
even substantially no oxygen in chlorine evolved at the anode.

In contrast where the coating is omitted cathode efficiencies of 85-88% and oxygen concentration of 1-2% by volume in the chlorine have been observed.

The following examples are illustrative :

EXAMPLE 1

5

The cation exchange membrane is a sheet having a thickness of 0.3 millimeters constituted by two layers of cation resin laminated together with an interlayer of polytetrafluoroethylene screen as mechanical support, one layer is

10 made of a copolymer of tetrafluoroethylene and perfluorovinylether sulfonyl fluoride (or acid) having an equivalent weight of 1100 and the other layer consisting of a copolymer of tetrafluoroethylene and a perfluorovinyleter containing carboxylic groups and having an equivalent weight approximately

15 in the same ranges.

It is sandblasted on the cathode surface represented by the layer or resin containing carboxyl groups by means of quartz particles having a size comprised between 50 and 150 microns, sprayed by means of compressed air at 5 atmospheres

20 pressure through a nozzle kept at 25 millimeters from the membrane surface.

The membrane is then hydrated by soaking in a deionized and distilled water for about 2 hours at a temperature from 60 to 80°C.

25 The membrane is then placed on the bottom of a watertight container consisting in a flat bottom and a frame laid on the perimeter of the membrane with the carboxylic side up. An aqueous solution containing 10% by weight of caustic soda is poured on the membrane at room temperature and left for

60 seconds. Then the solution is removed and the membrane surface was quickly rinsed with distilled water.

An aqueous solution 0.15 N of silver nitrate is then poured on the treated carboxylic surface of the sheet in the same container, at room temperature, and left for 60 seconds.

The membrane surface is rinsed again with distilled water and an aqueous solution containing 20% of hydroquinone is then poured on the sheet in the container and left for 10 minutes. A silver layer is deposited on the carboxylic side of the membrane coating the sulfonic acid side of the membrane uncoated. The weight of silver is about 0.5 grams per square meter of membrane surface.

The morphology of the silver layer deposited on the carboxylic side of membrane is then observed under an electronic microscope. The silver layer appears constituted by finely dispersed crystals having dimensions varying from 0.01 micron to 0.1 micron. The thickness of the silver layer substantially corresponds to the sizes of the crystals and the porosity degree, expressed as the ratio between full and empty spaces of the projected area, is comprised between 1.2 and 0.5 and ranges from 0.1 to 0.5 micron.

Figure 3 is an enlargement, magnified 80.000 times, of the silver electrode so deposited on the membrane.

For comparison purposes, Figure 4 shows an enlargement at a magnification of 10,000, of a palladium electrode obtained via following the reduction method disclosed in Example 1 of the Italian Patent application SN 20.489 A/80.

From the comparison of the two electrodic layers, it is clear that the palladium electrode obtained via "electroless" exhibits a typical structure of growth with large modular grains and agglomerates, several (about 10) micron thick and the membrane appears to be completely shielded by the metallic

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layers, conversely the silver electrode of the invention shows
a thinner structure characterized by finely dispersed smaller
grains with a high porosity degree.

The lateral resistivity of the silver electrodic layer
measured by a microhmeter is about 7 ohm centimeters.

EXAMPLE 2

The membrane/electrode system obtained according to the
method of the foregoing example, was arranged in a laboratory
cell similar to that illustrated in figs. 1 and 2 and consist-
ing of two compartments separated by the coated membrane with
the silver coating on the cathode side.

The anode was an expanded sheet of titanium, coated with
an electrocatalytic layer of titanium and ruthenium mixed oxide
supplied by Permelec S.p.A. of Milan, under the trade mark of
DSA(R). The low overvoltage cathode section was a micronet
with 9 meshes per cm., galvanically coated with an alloy of
nickel (50%) and ruthenium (50%), directly pressed against
the silver layer deposited on the membrane surface. Moreover,
the current conducting system comprised an undulating crimped
resilient mat about 0.5 centimeters thick made of knitted
nickel wire having a diameter of 0.11 millimeters pressed
against the micro-net by means of an expanded sheet made of
low-carbon containing steel, substantially rigid and connected
to the negative pole of the electric current source.

The electrode surface was about 240 x 240 millimeters.

Sodium chloride brine was flowed through the anolyte
chamber and electrolyzed under the following conditions :

- anolyte concentration	20 g/l of NaCl
- anolyte pH	4 to 4.5
- temperature	80°C

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- sodium hydroxide concentration in
the catholyte   25% by weight

- current density   3300 Amperes per
                                                  Square Meter

Under these conditions the cell operating data were as follows :

- Cell voltage between the external
connectors   Initial voltage 3.0
                                                  gradually rising to
                                                  3.32 volts

- Faradic efficiency on soda produc-
ion   97 %

Oxygen in the chlorine below 0.2 percent is observed in this type of experiment.

EXAMPLE   3

Further such cation membrane sheet have been coated on the carboxylic layer surface with silver electrode prepared according to the method described in Example 1, varying opportunely the conditions for controlling the quantity and therefore the thickness of the electrodic layer.

The conditions used for each sample and the relevant electrodic thicknesses obtained are listed in the following Table I.

TABLE I

Sample	Absorption in NaOH			Absorption in AgNO$_3$			Thickness of Silver Layer
	NaOH Conc. % by Weight	Temp. °C	Contact Time Sec.	Normality N	Temp. °C	Contact Time Sec.	MICRON
A	20	24	60	0.1	24	60	0.02
B	10	24	60	0.1	24	60	0.025
C	10	25	60	0.1	26	60	0.01
D	2.5	25	60	0.1	25	60	0.02
E	2.5	25	60	1	25	60	0.04
F	1	24	120	0.01	24	120	0.015
G	1	24	120	0.1	24	60	0.01

The various samples of Table I have been tested as membrane/cathode systems in the same cell and under the same conditions of Example 2, for the electrolysis of sodium chloride. The results obtained for each sample are listed in the following Table II.

TABLE II

Sample	Cell Voltage V	Caustic Soda Faradic Yield %
A	3.15	97
B	3.2	97
C	3.3	97
D	3.2	97
E	3.3	95
F	3.3	96
G	3.2	96

EXAMPLE 4

The membrane treated is a fluorocarbon polymer cation exchange membrane which is a laminate of two layers. One of these layers is a copolymer of a polyfluoroethylene (tetrafluoroethylene) and a perfluorovinylether sulfonylfluoride (or/and) having an equivalent weight of about 1100. The other layer is a sheet of a copolymer of the polyfluoroethylene (tetrafluoroethylene) and a perfluoroethylene other which contains carboxylic groups. This carboxylic sheet also has an equivalent weight of about 1100.

The two layers are laminated together with an interlayer of polytetrafluoroethylene screen to provide mechanical support.

The thickness of the membrane is 0.3 millimeters.

Square sheets of this type of membrane 10 centimeters by
10 centimeters are sandblasted on the carboxylic surface with
quartz particles ranging in size from 50 to 150 microns sprayed
by compressed air at 5 atmospheres pressure through a nozzle
maintained at a distance of 25 millimeters from the membrane
surface over a period of about 30 seconds. The carboxylic
surface of such sheets is thus roughened.

The treated sheet is assembled in different cells of
the type described above after conditioning by heating at
about 80°C in an aqueous solution containing 2-3 percent by
weight of sodium chloride until the dimensions of the sheet
(swelling) has stabilized.

The cell has anodes as described above comprising expanded
titanium metal with a ruthenium oxide coating thereon. A
ruthenium oxide coated titanium screen is interposed between
the expanded metal and the anode (sulfonic) side of the
membrane. The sheets are installed with the sandblasted
carboxylic surface on the cathode side. As illustrated in the
drawing and described above, the cathode comprises a cathode
backplate and pressure plate engaging a compressible knitted
metal crimped compressible mat 113 which compresses against
the screen or screens which in turn are pressed against the
membrane surface.

In two tests (Runs 1 and 2) a single screen is pressed
against the surface of the membrane by the compressible mat.
In other tests (Runs 3, 4 and 5) a spacer screen (second
screen) of relatively high hydrogen overvoltage is sandwiched
between the surface of the membrane and the low hydrogen over-
voltage first screen. The order of the arrangement of cathode
parts is : Pressure plate-mat-first screen-second screen-
membrane.

The cells are operated circulating aqueous brine containing 215 to 225 grams per liter of sodium chloride through the anolyte compartment and aqueous sodium hydroxide through the catholyte compartment with enough alkali hydroxide withdrawn and water added to the catholyte to maintain the hydroxide concentration at 30% by weight NaOH. Voltage imposed is enough to achieve the specified current density.

Results are obtained as stated in the following table with cathode and anode current efficiencies of 96% or above.

TABLE III

| Run | Surface Composition | | | | Observed Voltage (Volts) | |
-----	Pressure Plate	Mat Surface	First Screen	Second Screen	2000 Amperes per Square Meter	3000 Amperes per Square Meter
1	Nickel	Nickel	Nickel	–	3.26	3.58
2	"	"	Nickel Ruthenium Alloy	–	3.23	3.48
3	"	"	"	Nickel	3.11	3.41
4	"	"	"	Conductive Nickel Oxide Coating	3.12	3.38
5	"	"	Iron Sulfide	"	3.10	3.38

In these tests water circulation is controlled to produce 30% by weight of NaOH. Temperature of the cell was maintained at 65-70°C.

EXAMPLE 5

In a further series of tests membrane sheets 14 by 14 centimeters are sandblasted and assembled in similar cells with results as obtained in the following table :

5

TABLE IV

Run	Surface Composition				Observed Voltage (Volts)	
	Pressure Plate	Mat Surface	Firsts Screen	Second Screen	2000 Amperes per Square Meter	3000 Amperes per Square Meter
6	Nickel	Nickel	Nickel Ruthenium Oxide	Nickel	3.20	3.29
7	Iron	"	"	Nickel-Silver	3.10	3.19
8	Nickel	"	"	Nickel	3.16	3.24

10

15

In the above tests 30% by weight sodium hydroxide is obtained in tests 6 and 8 and 21-23 NaOH obtained in Test no. 7.

EXAMPLE 6

The following table summarizes results obtained in further

20 tests. The anode used comprised titanium screen pressed against a finer titanium screen which was pressed against the membrane. Both screens were coated with conductive ruthenium oxide. Sodium chloride solution containing 230 grams per liter of NaCl and having a pH of 3.5 was circulated at a temperature

25 of 65-75°C through the anolyte chamber. The current density was 3000 Amperes per square meter. In all the cases the membrane has been sandblasted on the cathode side with quartz particles for 30 seconds. The cathode alignment was as stated

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in table V. The results were as follows :

TABLE V .

Run	Surface Composition				Observed Voltage Volts
	Pressure Plate	Mat Surface	First Screen	Second Screen	
10	Nickel	Nickel	Iron Coated with Iron Sulfide	Nickel	3.25
11	"	"	"	One milimeter graphite cloth	3.68
12	"	"	"	Nickel Coated with Cadmium	3.32

The above process may be conducted in the electrolysis
of aqueous alkali metal chloride containing 150 to 325 grams·
per liter of alkali metal chloride and the amount of water fed
to the catholyte chamber being controlled to produce a
convenient concentration of NaOH ranging from 5 to 40 or more,
preferably 25 to 40 percent NaOH by weight. Other alkali metal
halides or other aqueous halides including hydrochloric acid
and other metal halides may be electrolyzed to produce the
corresponding halogens (chlorine, bromide include etc.).
Furthermore water may be electrolyzed with the cell herein
described to produce oxygen and hydrogen.

Although the present invention has been described with
particular reference to specific details of certain embodiments
thereof, it is not intended that such details shall be regard-
ed as limitations upon the scope of the invention, except
insofar as included in the accompanying claims.

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WHAT IS CLAIMED :

1. A method of generating halogen which comprises
electrolyzing an aqueous halide in an electrolytic cell having
a pair of opposed electrodes separated by an ion exchange
separator characterized in that at least one of said electrodes
has a first electroconductive electrolyte resistant surface
of relatively high overvoltage in contact with the surface
of the separator and a second electroconductive surface of
lower overvoltage in contact with said first surface.

2. Method for producing halogen by electrolysis of an
aqueous halide containing electrolyte in a cell comprising
an anode compartment containing an anode, a cathode compart-
ment containing a cathode and an ion permeable membrane
separating said compartments, characterized in that it
comprises providing an electrolyte and gas permeable foraminous
cathode having a first surface facing the catholyte side of
the membrane and a second surface directly adjacent to said
first surface on the side opposite to the side facing the
membrane, said second surface having a lower hydrogen over-
voltage than said first surface, imposing the same electrical
potential to both surfaces, while supplying water into the
catholyte compartment and brine in the anolyte compartment.

3. The method of claim 2, wherein said first surface has
a hydrogen overvoltage greater than the hydrogen overvoltage
of said second surface by a value comprised between 0.1 and
0.5 Volts.

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4. The method of claim 2, wherein the cathode is compris-
ed of a single foraminous layer of a cathodically resistant
base metal coated only on the side facing away from the
catholyte side of the membrane with a material having a lower
hydrogen overvoltage than the base metal.

5. The method of claim 2, wherein the cathode is compris-
ed of two separate layers, the first layer facing the catho-
lyte side of the membrane and the second layer superimposed
on said first layer and having a lower hydrogen overvoltage
than said first layer, both layers being maintained at the
same electrical potential.

6. The method of claim 5, wherein the first layer is
a porous silver coating on the cathode side of the membrane
having a thickness not in excess of 5 microns.

7. The method of claim 3, wherein said first surface is
the surface of a material belonging to the group of nickel,
iron, mild steel and silver and the second surface is the
surface of a material belonging to the group of nickel sulphide,
iron sulphide, nickel-ruthenium alloy, nickel-palladium alloy,
platinum, ruthenium and palladium.

8. The method of claim 2, wherein the said first surface
is in contact with the catholyte side of the membrane at a
plurality of points.

9. The method of claim 2, wherein the membrane is a cation
exchange membrane substantially impervious to hydrodynamic
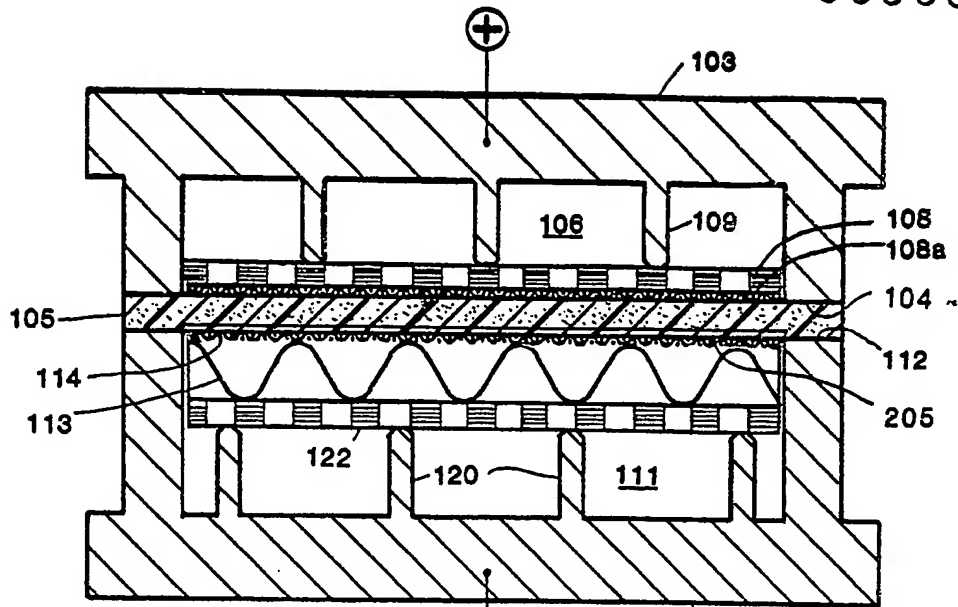flow of a perfluorocarbon carboxylic acid polymer.

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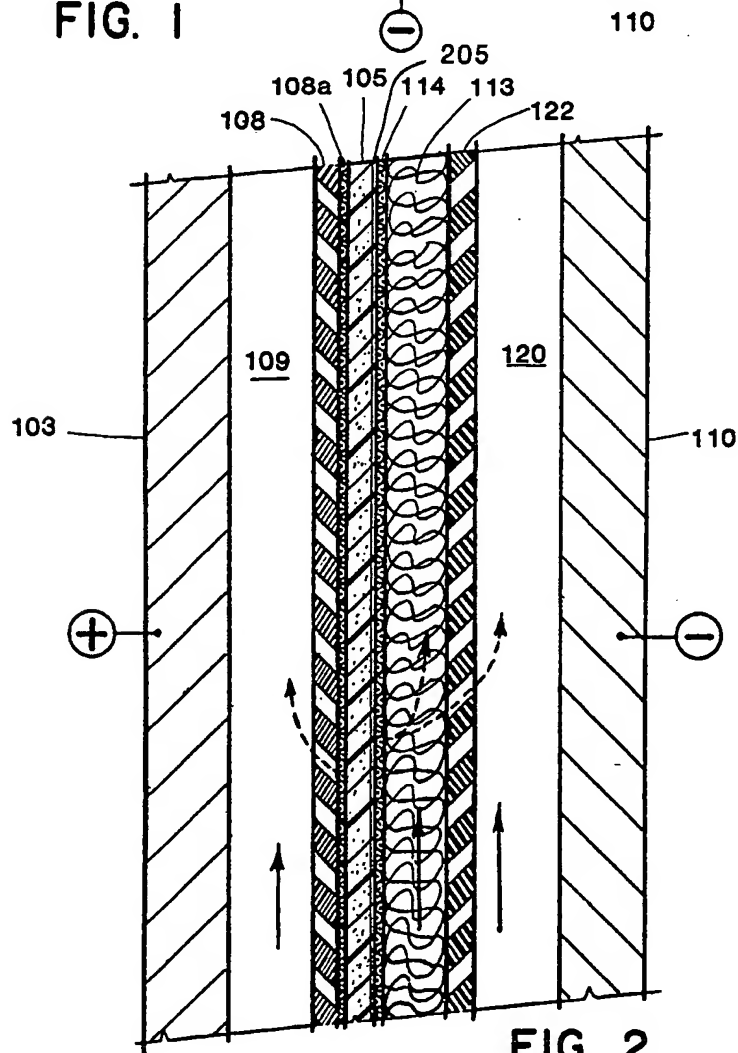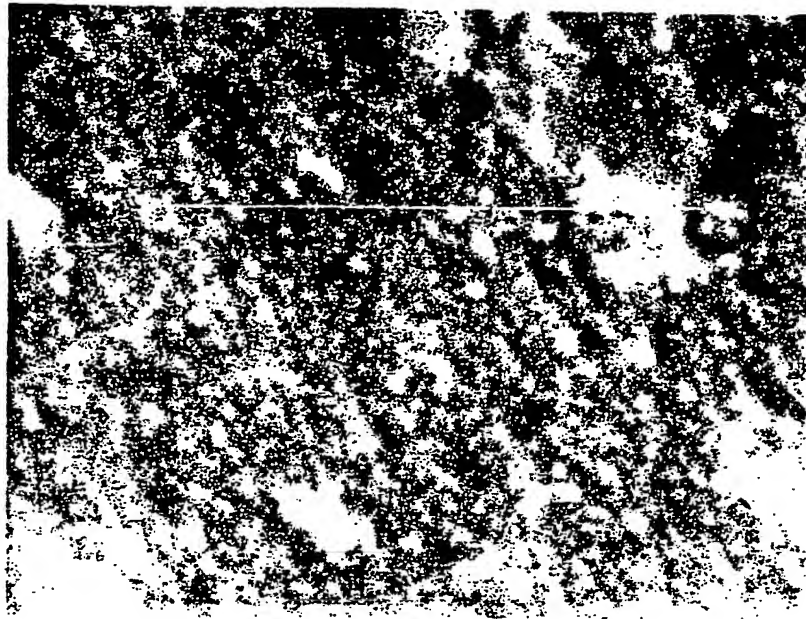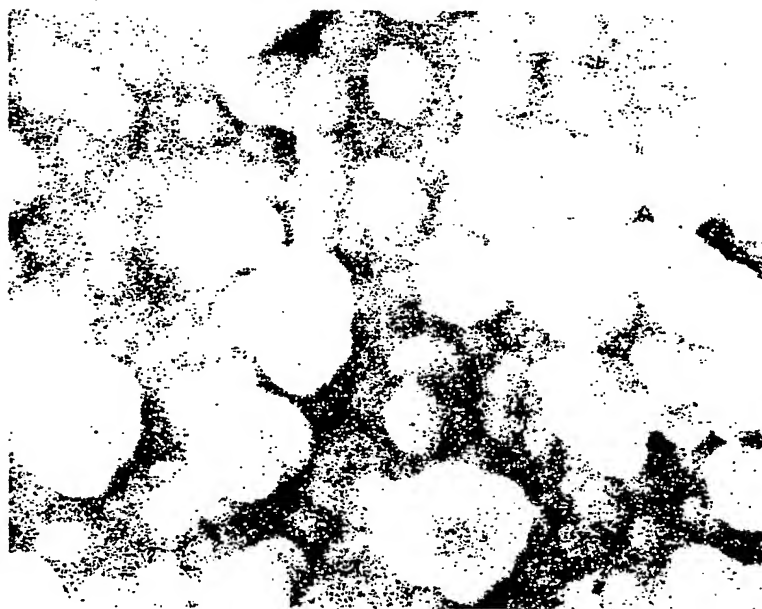
FIG. I

FIG. 2

FIG. 3

FIG. 4

European Patent
Office

EUROPEAN SEARCH REPORT

0050373
Application number

EP 81108662.8

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim
	GB - A - 1 534 942 (PORTALS WATER TREATMENT LIMITED) * Totality * --	1
	GB - A - 797 565 (LONZA ELECTRIC AND CHEMICAL WORKS LIMITED) * Totality * --	1
	US - A - 4 214 954 (HAN C. KUO) * Claims 1,3; column 1 * ----	1

DOCUMENTS CONSIDERED TO BE RELEVANT

CLASSIFICATION OF THE APPLICATION (Int. Cl.³)

C 25 B 11/00
C 25 B 1/46
C 25 B 9/00

TECHNICAL FIELDS SEARCHED (Int. Cl.³)

C 25 B

CATEGORY OF CITED DOCUMENTS

X: particularly relevant
A: technological background
O: non-written disclosure
P: intermediate document
T: theory or principle underlying the invention
E: conflicting application
D: document cited in the application
L: citation for other reasons

&. member of the same patent family, corresponding document

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
VIENNA	10-12-1981	HEIN

EPO Form 1503.1 06.78